SURFACE MODIFIED BISMUTH VANADATE IN PHOTOELECTROCHEMICAL SPLITTING OF WATER

A SYNOPSIS OF PROPOSED WORK SUBMITTED FOR

THE AWARD OF DEGREE OF DOCTOR OF PHILOSOPHY

IN CHEMISTRY

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1. Introduction

1.1 Alternative energy carrier

Excessive energy utilization by mankind is overfilling our surroundings with harmful green house gases such as carbon dioxide, ozone etc. due to the emission of carbon based fuels. About 85% of the energy comes from the burning of fossil fuels. However, fossil fuels are suspiciously spread over the planet and they are depleting at a very fast rate **[1].** We use 4.1 X 10^{20} J of energy per year which is equivalent to 15 TW of power. This consumption may be doubled by around 30 TW by the year 2050 and tripled by 46TW by the end of century **[2].** Therefore a tremendous research is going on in order to discover a clean and long-lasting renewable energy source. Among the various available renewable energy sources hydrogen is considered as a best energy carrier for future fuels **[3, 4].**

1.2 Hydrogen – As an energy carrier

Hydrogen is the first and lightest element in the periodic table. It is considered to be an energy carrier for the future as it is clean, odorless, colorless, nontoxic and most importantly it is environmental friendly as its combustion does not produce any greenhouse gas **[4].** Some important characteristics of hydrogen used as energy carriers are as follows-

- Energy density of hydrogen is much higher than any other fuel such as gasoline.
- Hydrogen has high heat of combustion (34.18 kcal/gm for H_2 and 10.30-10.33 Kcal/gm for petroleum).
- It has high energy storage capacity per mole (119000 J/gm for H_2 and 40,000 J/gm for oil).
- On combustion it does not produce any greenhouse gas.
- For one gram of hydrogen, ~140 kJ of energy can be released, which is almost four times higher than methane ~ 33 kJg^{-1}**[1, 3, 5, 6].**

1.3 Methods of hydrogen generation

Hydrogen is almost nonexistent on the earth therefore it is not a primary source **[4].** It is extracted from the different sources. Hydrogen can be produced from renewable and non renewable energy sources. The advantages of using former is that it is being environmentally friendly while later has either carbon di oxide or other green house gases as the byproducts **[7].** There are various methods available for the production of hydrogen such as steam reforming, electrolysis, fermentation, biomass, photoelectrochemical splitting of water **[8-9].** Among these available methods photoelectrochemical splitting of water is considered to be the best method.

1.4 Photoelectrochemical splitting of water

Photoelectrochemical (PEC) splitting of water for hydrogen production is also known as Artificial Photosynthesis. As in photosynthesis plant make use of solar light to split water and carbondioxide into oxygen and other carbohydrates, similarly photoelectrochemical cells use semiconductor as a leaf to split water into hydrogen and oxygen **[7, 10].**

Photoelectrochemical cell

The basic principle of photoelectrochemical cell is the conversion of light energy into chemical energy. Typical photoelectrochemical cell involves three electrodes namely as reference electrode, counter electrode and working electrode for the splitting of water. The possible arrangement of these electrodes in a PEC cell is as follows-

- Photoanode made of n-type semiconductor and photocathode made up of metal.
- Photoanode made up of n-type semiconductor and phocathode made up of p-type semiconductor.
- Photocathode made up of p-type semiconductor and photoanode made up of metal **[10].**

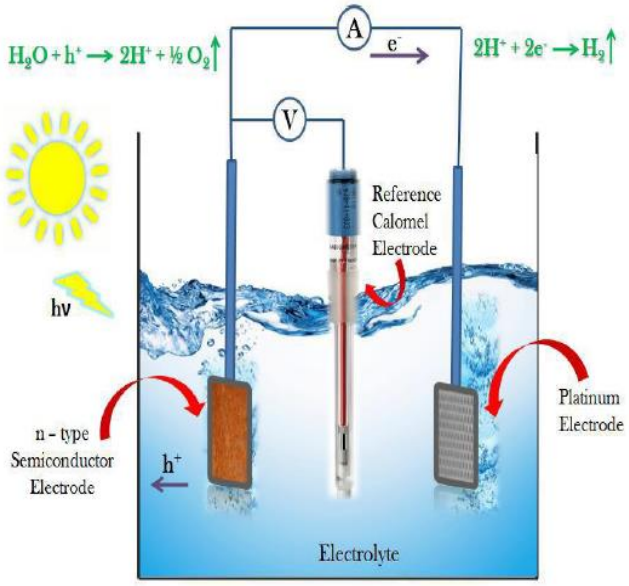


Fig. 1 Schematic diagram of a PEC cell

Reaction mechanism

When sunlight is incident on semiconductor electrodes, electron- hole pairs are generated. The photo excited electrons moves from valence band to conduction band and through the external circuit reaches to the counter electrodes where it reduces the H^+ ions. While holes reach to the semiconductor/electrolyte side where it oxidizes water. In this way we get hydrogen and oxygen at separate electrodes. The overall reaction mechanism is represented as **[7, 10-14]**

- **Photo absorption and charge carrier generation**

$$2h\upsilon \longrightarrow 2e^- + 2h^+ \quad \text{…. (1)}$$

- **Charge separation and transport**

Photoexcited electrons-holes pairs are separated and transported to the surface.

- **Oxidation of water by holes**

$$H_2O + 2h^+ \longrightarrow \tfrac{1}{2} O_2(g) + 2H^+ \quad \text{…. (2)}$$

- **Reduction of hydrogen ions**

$$2e^- + 2H^+ \longrightarrow H_2(g) \quad \text{…. (3)}$$

The overall reaction is given by-

$$2h\upsilon + H_2O \longrightarrow H_2(g) + \tfrac{1}{2} O_2(g) \quad \text{…. (4)}$$

Equation 4 takes place when energy absorbed by photoanode is either equal to or greater than the threshold energy (E_t)-

$$(E_t) = \frac{\Delta G^\circ(H_2O)}{2N_A}$$

Where $\Delta G^\circ(H_2O)$ is standard free energy and N_A is the Avogadro number **[10].**

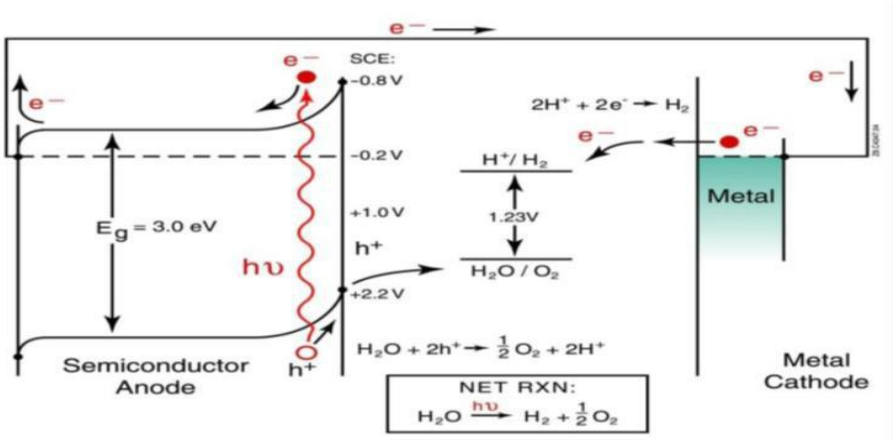


Fig. 2 working principle of a PEC cell

Thus,

$$E_i = h\upsilon = 1.23V$$

Thus, the electrochemical decomposition of water is possible when the electromotive force of the cell is equal to or greater than 1.23 V**[12].**

1.5 Semiconductor- The Heart of a PEC Cell

Semiconductor is considered to be the heart of PEC cell because it provides the charge carriers for driving the process of water splitting. Semiconductor are the solids whose electrical conductivity lies in the order of 10^{-9}-10^{-2} ohm cm **[1].** Two main requirements of a semiconductor used in a PEC cell is efficient absorption of visible light and good transport properties**[7,10,11,30].** Other required characteristics of a semiconductor for a PEC cell are listed below-

- Bang gap ˜1.8eV.
- Straddle water redox potential
- Long-term stability in aqueous electrolyte
- Durability > 2000h
- Low cost of Conversion efficiency > 10%
- Ease of maintenance

The pioneer experiment on photoelectrochemical cells was done by Fujishima and Honda in 1972. They worked on TiO_2 as the photoanode. Later on, many metal oxides (TiO_2, $SrTiO_3$, Fe_2O_3, Cu_2O etc.) and non metal oxides (GaAs, CdS, InP, etc.) have been used as photoanodes **[10, 17, 30].**

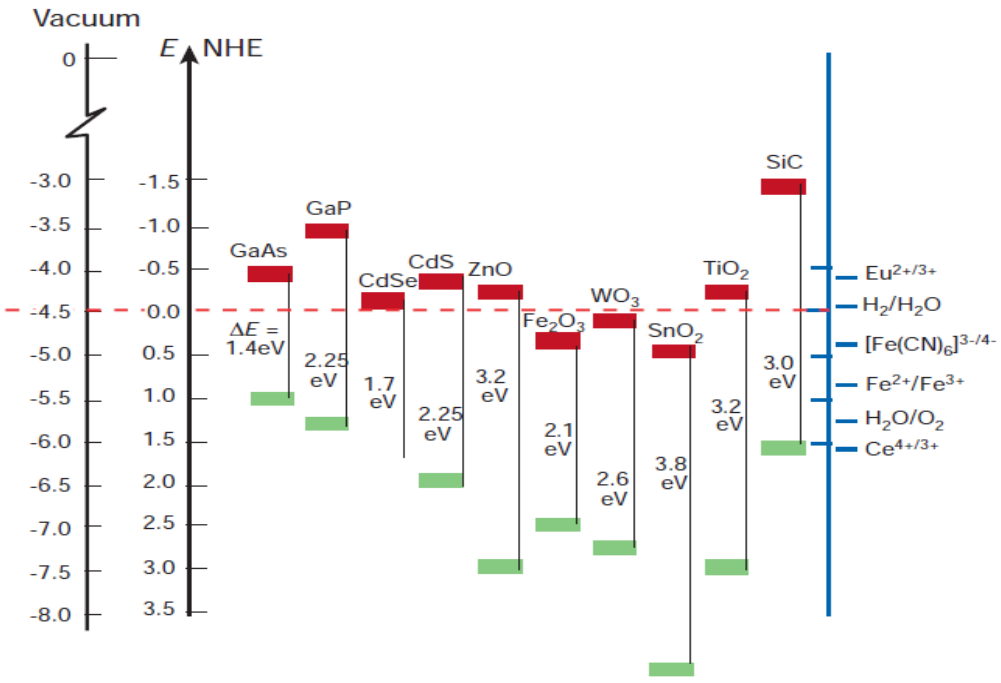


Fig. 3 Band Gap positions of different semiconductors [19]

1.6 Modifications attempted to enhance the PEC response

Heterojunction- A heterojunction is the combination of two semiconductor out of which one is high band gap material (UV absorber) and other one is smaller band gap material (Visible light absorber). When sunlight falls on this system both these layers absorb high energy photon and contributes to high photocurrent. The electron transfer takes place from low band gap material to high band material which results in enhancing the separation of charge carriers as well as prevent the recombination**[21-22].** In this way the highest photocurrent density may be achieved.

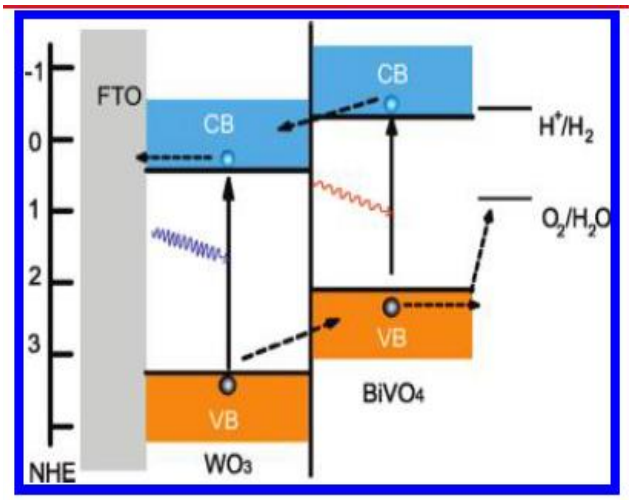


Fig. 4 Schematic diagram of $WO_3/BiVO_4$ heterojunction [20]

Diagram shows the heterojunction between $WO_3/BiVO_4$ in which electron transfer takes place from low band gap bismuthvanadate to high band gap tungusten trioxide which results in increasing the PEC response.

Doping- The introduction of impurities with in the semiconductor develop some energy level to enhance the visible light absorption capacity. Many dopants such as Si, Ge, W, V, Mo, Pt, Cu, Zn etc. have been used to increase the carrier concentratyion and conductivity which in turn increases the photoelectrochemical performance of the materials. W doped bismuth vanadate has been reported to increase the photoacitvity of $BiVO_4$ **[15, 24].**

Use of Co-catalyst- Poor water oxidation kinetics and inefficient charge transfer limitation of a semiconductor is improved by the loding of a cocatalyst. The main role of cocatalyst is to lower the activation energy of water oxidation by providing more efficient pathway of holes. It not only improve the photocatalytic activity but also increases the stability of a semiconductor material. Various cocatalysts such as Co-Pi, NiOOH, FeOOH, Ni-Bi etc. have been used in order to increase the stability as well as the PEC reponse**[14,16].**

Incorporation of Multiwall Carbon Nanotubes (MWCNT)- Incorporation of MWCNT within the semicoductor is expected to increase the PEC performace due to the long range Π- electronic configuration. Recent studies on MWCNT suggest that these nanotubes have excellent electrical, mechanical properties and large surface area for the storage of electrons **[26, 27].**

Upon illumination of a semiconductor electrode (metal oxide), valence band electron transfer to the conduction band and get trapped by the MWCNT which are then transfered to the conductive substrate. This quick transfer of electron from semicoductor to MWCNT results in efficient charge separation as well as increasing the performance of a PEC system**[25, 27].**

Swift heavy ion (SHI) irradiation- Energetic ion beams plays a vital role in the field of material science. Particle or ion beams which are accelerates from the accelerators are classified into two as low energy and high energy ion beams, depending upon the energy imparted to the materials. Low energy ion beams have energy from few KeV to few hundreds of KeV while high energy ion beams known as swift heavy ions (SHI) have energy from few tens of MeV to few GeV.

SHI impart energy via two process-

Nuclear energy loss- Direct transfer of energy to target atoms through elastic collisions.

Electronic energy loss- It occurs between incoming ions and electron of the target atoms Due to inelastic collisions.

SHI irradiation can be used to modify the structural, optical and optoelectronic properties of thin films. Such modifications, occurring at atomic and grain level, are expected to result in alteration of properties viz. band gap, resistance and structural defects, which are expected to enhance the photoelectrochemical response of the material **[23, 28, 29].**

A lot of work has been done on swift heavy ion in order to modify the properties of a material. Therefore, present work is an effort in order to change the structural, optical and electronic properties of bismuth vanadate using swift heavy ions. The use of SHI is expected to increase the PEC perform

2. Literature Review

Scientist from all over the world is working on photoelectrochemical splitting of water for the hydrogen production [1-11].

The work in the field of bismuth vanadate has been found from the last few years. Some of the recent work in this field has been given below-

J.H. Kim and J. S. Lee (2014) [13] discussed three different modification techhniques in $BiVO_4$ including heterojunctions with another semiconductor, addition of a charge transfer mediator and loading of a co catalyst in order to enhanced the PEC performance. They also compared the results of various heterostructuring techniues for $BiVO_4$.

K. Sayama et al. (2003) [14] prepared $BiVO_4$ thin film by metal organic decomposition using bismuth 2-ethylhexanoate and vanadium (oxy) acetylaacetonate in acetylacetone as the precursor solution. They found that nanocrystalline $BiVO_4$ thin film on conductive glass showed excellent IPCE (29% at 420nm) for decomposition of water.

X. Wan el al. (2013) [15] studied nanoporus bismuth vanadate modified with W doping as well as graphene surface reduced modification as an efficient photoanode in photoelectrochemical water oxidation. They found that photocurrent of modified W-$BiVO_4$/RGO incresed 3.96 times than pristine $BiVO_4$. Through the EIS measurment they observed that there is increase in donor density and decrease of charge transport and transfer resistance.

S. Hernandez et al. (2016) [16] discuss the preparation of $BiVO_4$ by spin coating method and also studied the influence of different film morphology (porous and dense) on the physiochemical and photoelectrochemical (PEC) performnace of the $BiVO_4$ photoanode for water splitting reaction. They also photodeposited CoPi cocatalyst on $BiVO_4$ to increse the efficiency of $BiVO_4$ and found that a photocurrent of 3mA/cm2 at 1.23 V vs. RHE under neutral pH has been achieved. Charge transfer kinetics of $BiVO_4$ with and without CoPi has also been quantified.

S. Sun et al. (2014) [17] explained the photocatalytic activity of quantum sized $BiVO_4$ for pure water splitting under simulated solar light irradiation. They observed that hydrogen evolution propeties of quantum sized $BiVO_4$ is mainly ascribed to the negative shift of conduction band edge by a quantum confinment effect.

S. J. Hong et al. (2011) [18] discussed about the fabrication of $BiVO_4/WO_3$ hetejunction by layer by layer deposition on conductive glass. They combined the merits of two semiconductors i.e. excellent harge transport characteristics of WO_3 and light absorption capability of $BiVO_4$ for enhanced photoactivity. They observed that composite electrode with optimized composition of one top $BiVO_4$ layer and four WO_3 layers on FTO showed the highest photocurrent as compare to bare WO_3 and $BiVO_4$.

Q. Jia et al. (2012) [19] developed a facile fabrication of $BiVO_4$ thin films from an queous nitric acid solution of $Bi(NO_3)_3$ and NH_4VO_3, followed by modification with CoO to improve the phoelectrochemical properties. They found the $BiVO_4$ (s-m) showed a larger anodic photocurrent and this anodic photocurrent depend on the concentration of a precursor solution and calcination temperature.

J. Su et al. (2011) [20] discussed the synthesis of WO_3 (nanorod array)/$BiVO_4$ heterojunction by solvothermal deposition of WO_3 nanorod array films on FTO followed by subsequent deposition of $BiVO_4$ by spin coating method. They observed that heterojunction films exhibited enhanced photoconversion efficiency and increasing photocorrosionstability as compared to planar $WO_3/BiVO_4$ films due to high surface area and improved charge separation of the photogenerated charges at the $WO_3/BiVO_4$ interface.

A. Verma et al. (2017) [21] explain the effect of Au embedded nanoparticles (NPs) on $BiVO_4/Fe_2O_3$ heterojunction in PEC splitting of water. They observed that formation of a heterojunction enhances the charge separation and transfer while Au NPs possessing surface plasmon resonance which results in enhancing the photoelectrochemical response by transferring energy to metal oxide by hot electron transfer.

A. Srivastav et al. (2016) [22] investigate the effect of gradient doping of Ti on Fe_2O_3 photoanode in sunlight based water splitting for hydrogen production. They observed a highly improved phototresponse in comparison to the pristine samples and 2 fold enhancement in comparison to 2% Ti doped Fe_2O_3 when dopant concentration varied from low to high (0.5-8%).

X. Wan el al. (2013) [23] studied nanoporus bismuth vanadate modified with W doping as well as graphene surface reduced modification as an efficient photoanode in photoelectrochemical water oxidation. They found that photocurrent of modified W-$BiVO_4$/RGO incresed 3.96 times than pristine $BiVO_4$. Through the EIS measurment they observed that there is increase in donor density and decrease of charge transport and transfer resistance.

Summary of work done on bismuth vanadate:

Author	**Material + Modifications**	**Outcome**
J. H. Kim et al. [13]	$BiVO_4/SnO_2/WO_3$	3.04 mA cm^{-2} at 1.2 V/RHE
	Co-Pi/gradient doped W:$BiVO_4$	3.6 mA cm^{-2} at 1.2 V/RHE
	$BiVO_4$ + MWCNT	1.3 mA cm^{-2}
J. Su et al. [20]	WO_3 nanorod/$BiVO_4$ heterojunction	Due to the visible response of $BiVO_4$ and the improvement of charge separation in WO_3 nanorod/$BiVO_4$ heterojunction photocurrent increaes . thin films also showed increasing IPCE from 9.3% to 31% at 420 nm .
A.Verma et al. [21]	Au embedded $BiVO_4/Fe_2O_3$ heterojunction	Sample with 32% v/v Au solution in both layer gives best photoresponse i.e. 2.00mA cm^{-2} at 1V/SCE.

X. Wan et al. [23]	W doping and surface RGO modification on $BiVO_4$	Photocurrent for W-$BiVO_4$/RGO icreases by 3.96 times (1.39 mA cm^{-2}) compared to pure $BiVO_4$ (0.28 mA cm^{-2}) at 0.9 V vs Ag/AgCl due to enhnced charge carrier density and improved electronic conductivity.
W. Luo et al.[32]	RhO_2 loaded Mo-$BiVO_4$	Sea water splitting on RhO_2 loaded Mo-$BiVO_4$ corresponds to higher photocurrent (2.16 mA cm^{-2} at 1.0V RHE) due to enhanced conductivity and a increase hole diffusion length.
F.F. Abdi et al. [33]	Co-Pi: multi step gradient W doped $BiVO_4$	10 step gradient doped Co-Pi cocatalyzed W:$BiVO_4$ photoanode offer photocurrent density of 3.6mAcm^{-2} vs. RHE. On combining this system with a 2-jn a-Si solar cell photocurrent density increases and corresponds to 4.9% STH efficiency.
Y. Liang et al. [34]	FTO/SnO_2/$BiVO_4$:W	The external quatum efficiency (IPE) was improved by a factor of 7, leading to a highest IPCE of 46% at 450nm and 1.63 V/RHE.
J. A. Seabold et al. [35]	$BiVO_4$/FeOOH	$BiVO_4$/FeOOH exhibited significantly improved photocurrent and stability for photooxidation of water i.e. 1.0 mAcm^{-2} at 0.5V/RHE.
T. W.Kim et al. [36]	$BiVO_4$	Applying 2 different oxygen evolution

	$BiVO_4$/FeOOH $BiVO_4$/NiOOH $BiVO_4$/FeOOH/NiOOH $BiVO_4$/NiOOH/FeOOH	catalyst layers FeOOH & NiOOH reduces interface recombination which results in higher photocurrent density. $BiVO_4$/NiOOH/FeOOH photoanode achieves a photocurrent density of 2.73mA cm^{-2} at 0.6 V vs RHE.

3. Present Work

From the above discussion this becomes clear that $BiVO_4$ is a material of interest owing to its favorable properties such as low band gap around 2.4eV, good absorption in the visible region, good stability in neutral electrolyte, non toxic and straddle water redox potential. However it suffers from poor charge transport, electron hole pair recombination. Therefore, the present work is an attempt to apply some modifications such as loading of a dual co-catalyst i.e. CoAc & FeOOH, incorporation of Multiwall Carbon Nanotubes and application of swift heavy ions on Ni-doped Bismuth vanadate followed by formation of heterojunction with other semiconductors in order to enhance the efficiency of solar driven water splitting for hydrogen production **[17, 29-31].**

4. Objectives

1) Preparation of Bismuth Vanadate thin films by spray pyrolysis and electrodeposition method followed by doping and other modification viz. forming heterojunction & use of co-catalyst.
2) Characterization of the thin films by-

- X- Ray Diffraction techniques (XRD)
- Scanning Electron Microscopy (SEM)

- Atomic Force Microscopy (AFM);
- UV-Visible Spectrophotometer

3) Impedance analysis of the thin films by electrochemical impedance spectroscopy.
4) Mott-schottky analysis of the thin films to find out the flat band potential.
5) Study of phototelectrochemical behavior of the thin films under dark and illumination using different electrolyte.
6) Comparison of results obtained from samples prepared by different methods.

5. Methodology

5.1 Preparation of $BiVO_4$ thin films – $BiVO_4$ thin films will be prepared on FTO substrate using spray pyrolysis method and electrodeposition method.

5.2 Characterization of thin films–

Crystalline structure will be determined by XRD technique.

Morphology (particle size, shape, roughness) of thin films will be observed using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM).

Particle size – Particle size of $BiVO_4$ thin films will be determined using Scherrer's Equation ($0.9\lambda/\beta\cos\theta$).

Thickness of thin film – Thickness of $BiVO_4$ thin films will be measured by surface profilometer instrument.

Resistivity – Resistivity of the sample will be measured by resistivity meter. Current voltage relationship can also be used to determine the resistivity of the sample.

Band gap – Tauc plot band gap (Eg) will be calculated from the equation, which is given below Absorption coefficient, $\alpha = [A (h\nu - Eg)]/2$. This equation comes out from UV-Vis spectrophotometer.

Mott –Schottky Plot- Mott Schottky plot gives the information about band bending, flat band potential, donor acceptor densities using the equation –

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon_o \varepsilon N_D}\right)\left(V_{app} - V_{FB} - \frac{kT}{q}\right)$$

Where ε_o is the permittivity of the vacuum, N_D is the donor density, *Vapp* is the applied potential, ε is the dielectric constant of the semiconductor, *kT/q* is the temperature dependent term.

Impedance Analysis– Electron Impedance Spectroscopy (EIS) will give information about impedance and resistance at electrode electrolyte interface using Nyquist plot. In Nyquist plot, diameter of circle is directly related to the charge transfer resistance at semiconductor electrolyte interface.

Photoelectrochemical studies– PEC studies will be done using working electrode, Pt electrode and Calomel electrode using different electrolytes. I-V relationship of photoelectrochemical cells can be studied under both dark and illumination using *Zahner Electrochemical Workstation* and 300 W Xenon or Tungsten light source. Based on these information PEC response will be calculated.

6. Pilot work

Bismuth Vanadate thin films were synthesized by ultrasonic spray pyrolysis method using bismuth (III) nitrate penta-hydrate and vanadylacetylacetonate as the precursors. The precursor solution was prepared by mixing equimolar mixture of bismuth (III) nitrate penta- hydrate and vanadylacetylacetonate in acetic acid. The solution was sprayed by ultrasonic spray pyrolysis unit (Multiple Feed Spray Pyrolysis) using different flow rate(3-5 ml/min) at a temperature of 300˚C. The deposited films were finally annealed at 450˚C. Resulting thin films were bright yellow in color.

1. Phase analysis of the thin films was carried out using X-Ray diffractometer (**Bruker AXS D8 Advance)**. The prepared thin films exhibit scheelite monoclinic phase corresponding to 2Θ values at 18.8˚, 28.9˚, 31˚. All these values matches with the JCPDS card no.01-075-1867.

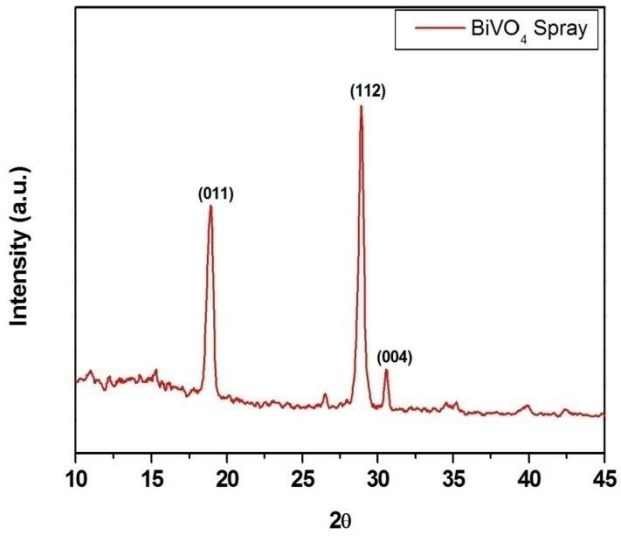


Fig. 5 XRD pattern for the prepared thin films

2. Photoelectrochemical studies of the thin films were carried out using three electrode systems viz. counter electrode, reference electrode and working electrode. The applied potential for the process is -1.0 V to 1.0 V vs. SCE. The PEC analysis was carried out both in dark and under light illumination using sodium hydroxide as an electrolyte. The results are as follows:

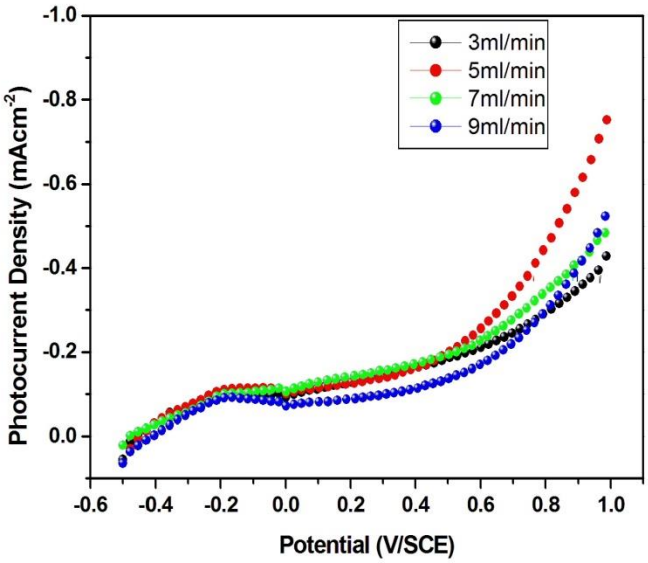
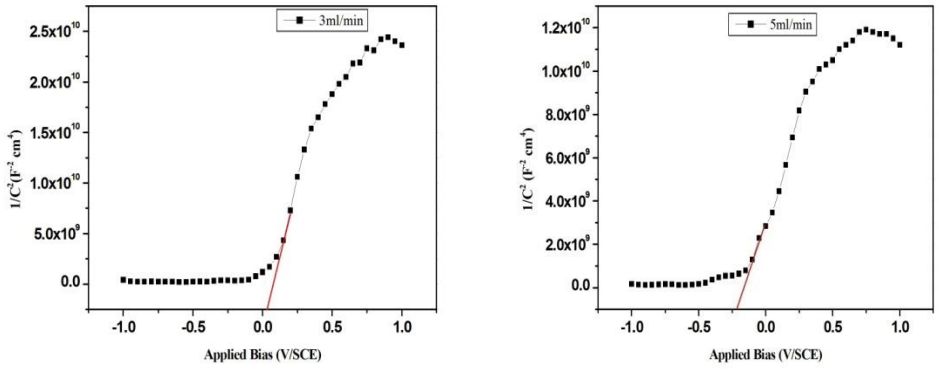


Fig. 6 Photocurrent density plot for the prepared thin films

Flow rate (ml/min)	Dark Current (mA)	Light Current (mA)	Photocurrent Density ($mAcm^{-2}$)
3	0.0045	0.43	0.42
5	0.0065	0.75	0.75
7	0.006	0.50	0.49
9	0.0059	0.53	0.51

3. Mott- Schottky analysis of the prepared thin films was carried out in order to find out the flat band potential. Fig. 7 shows the mott-schottky plots for $BiVO_4$ thin films prepared at different flow rates. From the Fig. it is clear that the film prepared with 5ml/min flow rate has the highest negative flat band potential.



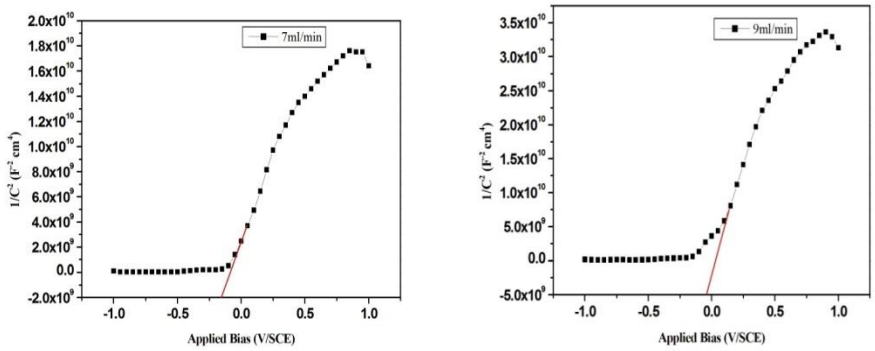


Fig. 7 Mott- Schottky plots for $BiVO_4$ prepared at different flow rates

Flow Rate (ml/min)	Flat band potential
3	0.025
5	-0.21
7	-0.15
9	-0.04

4. UV-visible spectrum of $BiVO_4$ thin films prepared at different flow rates using ultrasonic spray pyrolysis setup are shown in Fig. 8. From the fig. it was clear that the absorbance increases with the flow rate and it was found to be maximum at a wavelength of 331- 346.0 nm. The absorbance for samples prepared at different flow rates are given below-

Flow Rate (ml/min)	Absorbance (a.u.)	Wavelength (nm)
3	2.74	346.0
5	3.6	345.0
7	4.38	347.1
9	5.01	331.7

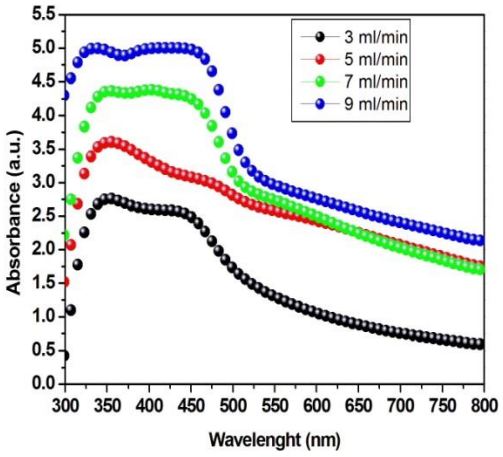


Fig. 8 UV-VIS spectrum for $BiVO_4$ prepared at different flow rates

5. Tauc plot for the $BiVO_4$ samples prepare at different flow rate are shown in Fig. 9. The band gap for different samples lies in the range from 2.0 to 2.2 eV.

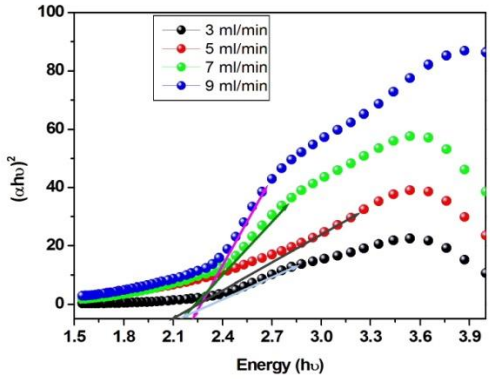


Fig. 9 Tauc plot for $BiVO_4$ prepared at different flow rate

Flow rate (ml/min)	Band gap (eV)
3	2.14
5	2.08
7	2.14
9	2.21

7. Expected Outcome

The present work is proposed to overcome the limitations such as poor charge transport and electron-hole pair recombination associated with $BiVO_4$ and the expected outcomes are

- Formation of heterojunction with low & high band gap materials may facilitate separation of charge carriers and prevents back recombination.
- Doping of transition metals (Mo, W, Pt etc.) is expected to increase the conductivity as well as photoelectrochemical performance.
- Use of Co-catalysts (Co-Pi, NiOOH , FeOOH etc.) is expected to lower the activation energy of water oxidation by providing efficient pathway to holes thereby enhancing the stability as well as PEC performance.

All these above mentioned modifications are expected to increase the PEC performance of $BiVO_4$ and will augment the efficiency of hydrogen generation.

8. References

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